S. Y. B. Pharm.SemIII- QP 27661

Q.1 A] Answer the following questions:

A) Assign E/Z or R/S or D/L notations and nomenclate the following molecules as per IUPAC rules [04]



B) Draw structural formula for the following compounds

i) (S)- 3-Amino-3-methyl-4-hexen-2-one



ii) (E)-1-Phenyl-2,3,3-trimethyl-1-butene



iii) (R) 2,3- dihydroxypropanal



iv) ethyl 3-butenoate



Q.1 C) Answer the following questions (Choice 6 out of 7) (12Marks)





ii. Write resonating structures for the following molecule and give the order of stability





iii. Represent Fischer, Wedge, Newman and Sawhorse projection formulae for the 3-Amino-3bromo-2-methylpentanal



iv. Identify the relationship between two chiral structures



v. Give the structure of conjugate acid/base of the given molecules

methyl amine $(CH_3NH_3^+, its conjugate acid)$ and hydrochloric acid ($CI^-: conjugate base$) vi. Identify the electrophiles and nucleophiles (including charged and neutral species) in the given reactions



[Nucleophile methanol and electrophile leaving group]

OR

 $H:CI + H_2C = CH_2 \longrightarrow f = CI^{\ominus}$

[The concept of an acid as a proton donor (HCl) and a base as a proton acceptor (ethene) is due to Bronsted and Lowry (1923), ethane cation : electrophile and Cl- nucleophile]

vii. What is the order of stability of carbocations? Justify the same.

Q.2.

i. Draw the molecular orbital energy diagram for ketone. Label the orbitals.

2M



ii. Identify the hybridization state of the underlined atom from the given molecule.

(Hybridization States of C, O, N (Ref: Clayden) C1=SP3; C2= SP, C4=SP3, C5=SP2





iii. List the following alkyl halides in decreasing order of S_N2 reactivity. Justify your answer.

i)
$$CH_3$$
 ii) CH_2Cl iii) CH_2Cl

Propose the mechanism of the most active compound with alcoholic NaOH. (04)

ie primary alkyl halides are more reactive than secondary, which in turn are more reactive than tertiary towards an $S_N 2$ reaction. (2 marks: 1 mark for the correct order, 1 mark for the justification)

The $S_N 2$ mechanism of ii with alcoholic NaOH should therefore be written in details. (2 marks for the mechanism, including discussion of the transition state, which justifies the order of reactivity)

iv. Neatly draw and label the energy profile diagram to depict the following reactions and identify and draw the transition state/s and define an equilibrium constant for the same.



Q.3

i. Discuss:Bayer strain strain in cycloalkanes

Bayer strain

In 1890, the famous German organic chemist, A. Baeyer, suggested that cyclopropane and cyclobutane derivatives are different from cyclopentane and cyclohexane, because their C—C—C—C angles cannot have the tetrahedral value of 109.5°. In cycloalkanes, each carbon is bonded covalently to two carbons and two hydrogen. The carbons have sp3 hybridization and should have ideal bond angles of 109.5°. Due to the limitations of cyclic structure, however, the ideal angle is only achieved in a six carbon ring — cyclohexane in chair conformation. For other cycloalkanes, the bond angles deviate from ideal.

2M

Discuss the chirality of the following compounds and Justify



ii. Give the stable active intermediate/s for the given moiety and cite the reason for its stability



iii. Complete the following reaction and suggest the mechanism



E1 reactions also are regioselective and follow Zaitsev rule



iv. Write a note on and comment on the stereochemistry of the product. 4M

OR



Q. 4 i. Suggest suitable strategies to make the equilibrium favor in the given below esterification reaction. Discuss the relationship between energy, enthalpy and entropy.



ii. a. Which one of the following pair is expected to exhibit H-bonding and why. Justify your answer

Ethanol and diethylether 2M

(Schaum Series Chapter 7 pg108) Ethanol, diethylether (Ans Ethanol)

b. On the basis of solubility, justify the increasing order of logP for the following compounds 2M

Phenol (logP=1.5), benzene (logP=2.1), chlorobenzene (logP=2.9)

Ans: H-bonding with compounds and solubility of compounds in organic phases

iii. Attempt the following conversions

a. acetophenone to acetic acid {using NaOH---haloform---acid} [Ans. to this question would be benzoic acid and not acetic acid, hence examiner can give one marks if this question is attempted by the candidate]

4M

- b. Benzoyl chloride to ethyl benzoate {schotten Bauman}
- c. Benzyl chloride to benzoic acid {oxidation reaction with sodium dichromate, H2SO4}

d. Phenyl ethyl ether to phenol {cleavage of ether linkage using HI/HBr reagent gives alcohol and alkyl halide}

Q.5 i. Write the order of acidity between acetic acid, fluoroacetic acid, difluoroacetic acid and trifluoroacetic acid and justify



Least to most acidic compounds due to electron withdrawing inductive effect.

ii. Give an example to justify following statement - Delocalization of the negative charge stabilizes the conjugate base





the negative charge on the perchlorate anion is delocalized over all four oxygens



ii. B] Name the least stable and most stable conformation of cyclohexane and justify your answerby drawing the energy profile diagram4M



$$TC = twist chair$$

 $B = boat$
 $TB = twist boat$
 $C = chair$

iii. Enlist examples of the functional groups which are responsible for Dipole- dipole OR hydrophobic interactions. Suggest a suitable modification of this group which will enhance or decrease this interaction





OR

Read Patrick Book

Q.6 i. With the help of suitable example explain kinetic Vs thermodynamically controlled reactions 4M



The two alkenes are labelled E and Z. After about 2 hours the main product is the Z-alkene. However, this is not the case in the early stages of the reaction. The graph below shows how the proportions of the starting material and the two products change with time.



Points to note:

• When the alkyne concentration drops almost to zero (10 minutes), the only alkene that has been formed is the *E*-alkene.

KINETIC VERSUS THERMODYNAMIC PRODUCTS

- As time increases, the amount of *E*-alkene decreases as the amount of *Z*-alkene increases.
- Eventually, the proportions of *E* and *Z*-alkene do not change.

Since it is the *Z*-alkene that dominates at equilibrium, this must be lower in energy than the *E*-alkene. Since we know the ratio of the products at equilibrium, we can work out the difference in energy between the two isomers:

ratio of E:Z-alkenes at equilibrium = 1:35

$$K_{\rm eq} = \frac{[Z]}{[E]} = 35$$

 $\Delta G = -RT \ln K = -8.314 \times 298 \times \ln(35) = -8.8 \text{ kJ mol}^{-1}$

that is, the Z-alkene is 8.8 kJ mol⁻¹ lower in energy than the E-alkene.

However, although the *Z*-alkene is more stable, the *E*-alkene is formed faster under these conditions: the route to the *E*-alkene must have a smaller activation energy barrier than *trans* addition. This is quite easy to understand: the intermediate cation has no double-bond geometry because the cationic C is sp hybridized (linear). When chloride attacks, it prefers to attack from the side of the H atom rather than the (bigger) methyl group.

■ You might normally expect an *E*-alkene to be more stable than a *Z*-alkene—it just so happens here that CI has a higher priority than Ph and the *Z*-alkene has the two largest orouus (Ph and Me) trans (see



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This information can be summarized on an energy profile diagram:



- Kinetic and thermodynamic products
 - The E-alkene is formed faster and is known as the kinetic product or the product of kinetic control.
 - The Z-alkene is more stable and is known as the thermodynamic product or the product of thermodynamic control.
- ii. Identify the given molecules are aromatic, nonaromatic or antiaromatic

4M



iii. Write $1^{\circ}, 2^{\circ}, 3^{\circ}$ aromatic amine distinguishing test by giving suitable examples

4M

Diazotization test refer Morrison and Boyd